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MECHANICAL PROPERTY CHANGES IN ION IRRADIATED METALS - PART II: HIGH STRENGTH Cu-Ni-Be ALLOY

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ABSTRACT

Mechanical property changes in a high-strength copper alloy as a result of 14 MeV Cu ion irradiation have been investigated using a recently developed Mechanical Properties Microprobe (MPM). A Cu-1.5% Ni-0.3% Be alloy was irradiated in both the cold worked and aged, and solution annealed and aged conditions, to a peak damage dose of 40 dpa (10 dpa at 1 μm) over the temperature range of 100°C to 500°C. Ultra-low load microindentation hardness changes were measured parallel to the ion beam and perpendicular to the beam, the latter being made possible by cross-section techniques. Both thermal and radiation-enhanced softening was observed in the cold worked and aged material and the amount of softening increased as temperature increased. Irradiation had very little effect on the solution-annealed and aged material and only at 500°C was any thermally-induced softening observed.

INTRODUCTION

The high damage rate of heavy ion irradiation has made it a useful tool in the study of the effect of irradiation to high damage levels in copper alloys[1-4]. However, until recently only neutron irradiations have been used in the investigation of radiation effects on mechanical properties in these alloys[5-7]. The limited damage region of heavy ion irradiation (typically ~ 1 μm deep) limits the usefulness of conventional mechanical property tests. Recently a new technique has been developed which allows for direct measurements of mechanical properties in this narrow damage zone[8]. This technique has been used to investigate thermal and heavy ion irradiation effects on the hardness and elastic modulus of a Cu-Ni-Be alloy.

EXPERIMENTAL

High purity Cu-1.5% Ni-0.3% Be was received in the 20% cold-worked and aged condition[9]. Some of the alloy was solution annealed at 950°C and then aged for three hours at 482°C. Samples, of dimension 5 x 10 mm, were mechanically polished to a 0.05 μm finish and then electropolished in a solution of 67% CH_3OH and 33% HNO_3 at 5 V and -40°C. Irradiation with 14 MeV Cu^{3+} was done using the tandem accelerator facility at the University of Wisconsin-Madison. The irradiations were done over the temperature range of 100-500°C to 10 dpa at 1 μm (40 dpa at peak) to a maximum depth of about 3 μm[3]. The samples were masked such that only a 3 mm diameter area was irradiated. Irradiated samples for cross-sectional analysis were prepared using standard techniques[10]. These electroplated samples were mechanically polished to a 0.05 μm finish and the surface electropolished at -30 to -40°C for 2 to 3 seconds in preparation for the microindentation hardness testing.

Hardness measurements were performed using the techniques described in Part I of this series. Modulus measurements were made on these specimens using the MPM. The initial slope of the unloading curve (see Part I, Figure 2) is proportional to the plastic depth (d_p) and the modulus (E). Details of the analysis of the unloading curve are given elsewhere[11,12].

Indentations were made both normal to the irradiated surface (on as-irradiated specimens) and parallel to it (on cross-section specimens). The normal indentations were made in both irradiated and unirradiated areas to depths of 500 and 1500 nm before unloading at a constant displacement rate of 5 nm/s. Ratios were calculated of these hardness values to values corresponding to the pre-irradiated states. Cross-section specimens were indented and hardness ratios calculated in the same manner as the specimens in Part I of this series.

RESULTS

Table 1 shows the initial mechanical properties of the samples. The yield strength was measured prior to receiving the alloy[9]. The modulus measurements represent a comparison of values found in the literature using conventional tests[13] and those measured on the MPM, which have about a 10% error. The nanohardness measurements were made on the MPM and represent loads of about 10 g. The Vickers microhardness and the MPM nanohardness values have comparable standard deviations of less than 5%.

Hardness ratios for indentations made normal to the irradiated surface are presented in Fig. 1. Cu-Ni-Be experiences softening in both of the heat-treatment conditions. The softening appears to begin at 300°C for the cold-worked and aged condition and is more pronounced in the irradiated region with hardness losses of up to 25%. For the solution-annealed and aged condition only the 500°C sample experiences softening, with little difference between the irradiated and unirradiated regions. The hardness ratios, calculated from the loading data, for all irradiated samples were relatively constant from a depth of about 300 nm to 1.5 μm and were identical to those calculated at 500 nm and 1.5 μm from the unloading data. Both 500°C samples showed a dramatic drop in their ratios for depths less than 300 nm.

Ratios of irradiated to unirradiated bulk hardnesses made in cross-section are shown in Figs. 2 and 3 for the solution-annealed and aged and the cold-worked and aged conditions respectively. In the solution-annealed and aged condition the ratios show about a 5% decrease in hardness in the irradiated region with about a 5% standard deviation. The 400°C cold-worked and aged sample shows almost no softening in the irradiated region, but the scatter of data is large with standard deviations of about 10% for many points. At 500°C the cold-worked and aged sample shows about a 15% decrease in irradiated hardness and a fair amount of scatter in the data.

Modulus measurements made on cross-section samples did not show any change in irradiated modulus relative to unirradiated. However, the spread in the data prevented any changes less than 15-20% from being discernible. Small 5-10% drops in modulus were seen in the 400°C cold-worked and aged sample and the 500°C solution-annealed and aged sample with indentations made normal to the surface. Surprisingly, the 500°C cold-worked and aged sample showed a distinct 30% drop in modulus in the irradiated region.

DISCUSSION

The hardnesses shown in Table 1 indicate that the solution-annealed and aged condition is stronger than the cold-worked and aged condition. This is due to the different solutionizing treatments that were employed for each condition. The cold-worked and aged samples were solution-annealed at 900°C prior to cold-working and aging(9). The solution-annealed and aged samples were solution-annealed at 950°C prior to aging in order to insure complete solution of the solutes. Solution-annealing at temperatures near 950°C prior to cold-working and aging has been shown to significantly increase the strength of this alloy ($\sigma_y \sim 900$ MPa)(13). Therefore, it is not surprising that using a much higher solution-annealing temperature yields a solution-annealed and aged hardness higher than a cold-worked and aged hardness using a conventional solution-annealing temperature.

The fact that the alloy in both conditions exhibits softening at 500°C is reasonable considering that this temperature is above the aging temperature (482°C) for this alloy. The cold-worked and aged condition is obviously more sensitive to irradiation and/or temperature than the other thermomechanical treatment. It appears that the cold-worked and aged condition overages very easily at temperatures over 300°C. Tensile tests on the two treatments of this alloy aged at 400°C for 1000 hours and neutron irradiated to 16 dpa at 450°C show a similar trend(5). Micron size precipitates were observed on the electropolished surface of the cold-worked and aged specimens at 400 and 500°C and none were observed in any of the solution-annealed and aged samples (see Figure 4). Microscopy of the neutron irradiated specimens(14) and of ion irradiated samples(4) shows that significant precipitate coarsening occurs in the cold-worked and aged treatment. Microscopy of irradiated cold-worked and aged Amzirc and MZC showed radiation-enhanced recovery and recrystallization and was attributed to radiation-induced diffusion which accurately predicted the enhancement of recrystallization[2,15]. The irradiation conditions of this study are similar to the Amzirc/MZC study, thus recovery and recrystallization should be expected. The decreases in hardnesses observed in the cold-worked and aged samples are similar to those found in recovered and recrystallized Cu-Ni-Be[16]. Radiation-enhanced recovery and recrystallization of the cold-worked and aged treatment was observed in ion and neutron irradiated specimens[4,14]. Further optical and electron microscopy will have to be performed on the specimens in this study to confirm these processes.

Hardness (H) can be related to yield strength (σ_y) by, $H \sim C\sigma_y$ (where C is usually taken to be 3 for Vickers indentations)[17-19]. The change in yield strength can be related to the change in hardness by:

$$\Delta\sigma_y/\sigma_y \sim \Delta H/H$$

or

$$\Delta\sigma_y \sim \sigma_y(H_f/H_i - 1),$$

where H_f/H_i is the hardness ratio of irradiated and/or aged samples to samples with only the initial treatments and is independent of C. Using this relationship it was found that the solution-annealed and aged sample at 500°C had a drop in yield strength of 140 MPa in the aged and the irradiated zones. The 400°C cold-worked and aged sample dropped 80 MPa in both areas, while the 500°C sample lost 120 MPa in the aged area and 200 MPa in the irradiated zone. The trends are similar to those found in the neutron study[5]. The yield strength dropped far more in the neutron study than in this study;

however, the times spent at temperature are vastly different (~ 1000 hours[5] versus < 10 hours respectively).

Various factors affect the hardness values measured in this study. Hardness measurements include contributions from the sample from depths up to 10 times the indentation depth[20]. However, the major fraction of the hardness comes from much shallower depths (3 to 4 times the indentation depth). Thus normal indentations to 500 nm should represent hardness contributions of the irradiated zone (~ 3 μm deep) almost entirely. Also the actual area that contributes to the hardness is larger than the indentation area[20] (~ 1 μm^2 for a 150 nm deep indent). Therefore, both modes of indentation are sampling a wide range of dpa values at any given depth, and any dpa related hardness changes will be dampened. Considering that dpa varies from less than 10 dpa to about 40 dpa in the irradiated zone, it is still surprising that the hardness ratio for normal indents from 500 to 1500 nm deep and for cross-section indents > 75 nm deep are constant in the irradiated zone. Part I of this study and a previous study using this technique found similar results [8]. With the hardness ratios of both methods being constant through the irradiation zone, it would indicate that the microstructural factors that contribute to hardness are independent of dpa level for a given ion fluence (~ 3×10^{20} ions/m^2).

Indentations were made normal to the irradiated surface and perpendicular to it in cross-section in order to compare the two methods. Table 2 shows that for hardness measurements there is close agreement for the alloy with both treatments. The error for the cold-worked and aged condition is much larger than for the solution-annealed and aged condition, particularly in cross-section. Problems were encountered indenting the former because of the micron size precipitates which are about the same size as the cross-section indentations. This can be seen in Fig. 4. The hardness values and their associated standard deviations do not include indentations made directly on a precipitate, of which a number were made in the cold-worked and aged samples. If these indentations were included the ratios would be different and their standard deviations would be much larger. Normal indentations of 500 nm or greater depth are not as severely affected by the coarsened precipitates.

For modulus measurements the scatter in data for the cross-section indentations made any conclusive trends impossible to detect. For the normal indentations a significant change in modulus was observed only in the irradiated zone of the 500°C cold-worked and aged specimen where it was seen to drop ~ 30%. The irradiated modulus is, within the standard deviation of the data, about the same as pure copper. This was seen in one other study using this technique where recovery and recrystallization occurred during the irradiation[8]. Modulus drops have been reported in stainless steels and have been attributed to swelling[21,22]. Voids have been observed in this alloy in recrystallized regions following irradiation[4,14]; however, without gas co-implantation this alloy is not expected to show any significant void formation under ion irradiation. The reason for such a large drop in modulus is not known at this time.

CONCLUSIONS

A moderately high dislocation density (20% cold-work) appears to accelerate softening in Cu-Ni-Be when it is exposed to temperatures of 300°C or more. Overaging is further accelerated when irradiation is included for the cold-worked condition. When the alloy is only aged following solution-annealing, neither temperature nor irradiation affect the hardness, unless the alloy is exposed to temperatures higher than the aging temperature of 482°C. For exposures over the aging temperature irradiation has little effect beyond thermal overaging for the solution-annealed and aged treatment. In either case even short term exposure to temperatures only slightly above the aging temperature results in rapid overaging and should be avoided. This study coupled with the neutron results indicates that the solution-annealed and aged condition has a far better response to irradiation at elevated temperatures than its cold-worked and aged counterpart.

Indentations made normal to the irradiated surface yield results similar to indentations made parallel to the surface in cross-section. This is possible as long as the hardness does not vary with dpa through the irradiated zone for a given ion fluence, and the irradiated zone is deeper than 2 to 4 times the normal indentation depth and 2 to 3 times the width of the cross section indentation. Consistent results for indentations become difficult when features about the same size as the indentation are present. Coarsening in the cold-worked and aged sample resulted in precipitates the same size as the indentations made in cross-section which made data analysis more difficult due to the large scatter in data.

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Table 1. Initial Mechanical Properties of Cu-Ni-Be in GPa

Thermomechanical Treatment	Yield Strength	Youngs Modulus Standard[15]	Youngs Modulus MPM	VHN (200g)	MPM (1500 nm)
Cold-worked & Aged	0.78[9]	140	160	2.20	3.10
Solution-annealed & Aged	—	140	160	2.35	3.45

Table 2. Ratios of Hardnesses in the Irradiated Zone to Hardnesses in the Unirradiated Zone

Thermomech. treatment	Temp (°C)	Normal	Cross-section
Cold-worked & aged	300	0.97±0.03	0.95±0.04
	400	0.98±0.03	0.95±0.04
	500	0.97±0.03	0.94±0.04
Solution-annealed & aged	400	0.95±0.05	0.98±0.10
	500	0.87±0.05	0.85±0.07

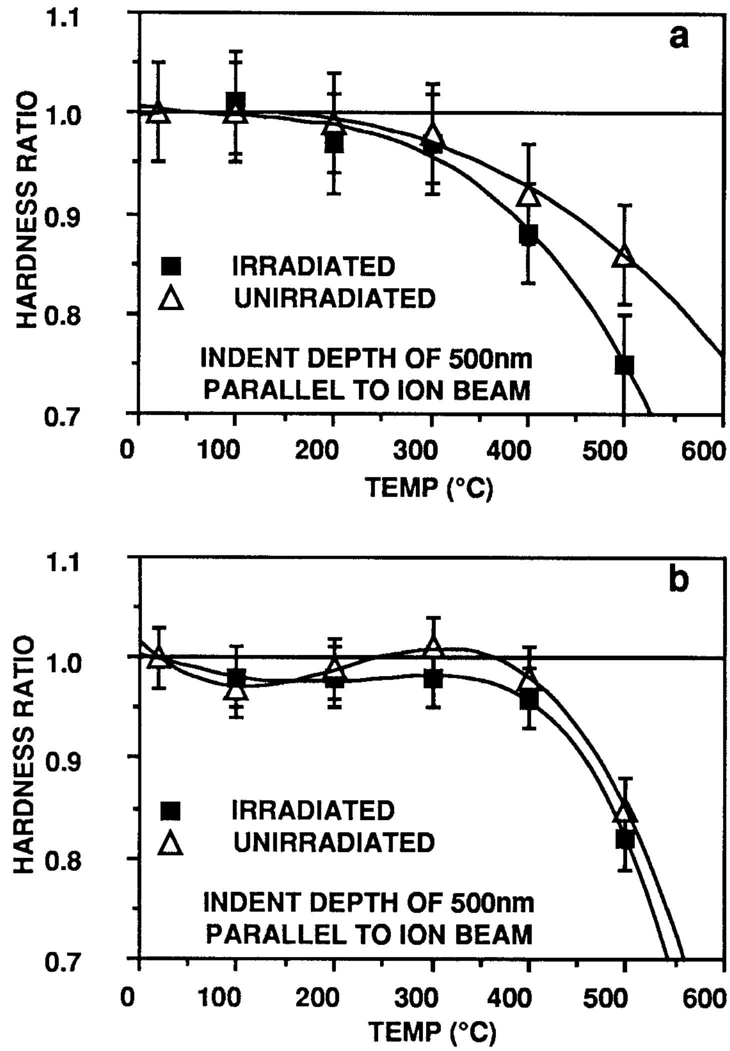

Fig. 1—Ratios of irradiated and unirradiated hardness to original hardness as a function of irradiation temperature for cold-worked and aged (a) and solution-annealed and aged (b) Cu-Ni-Be.

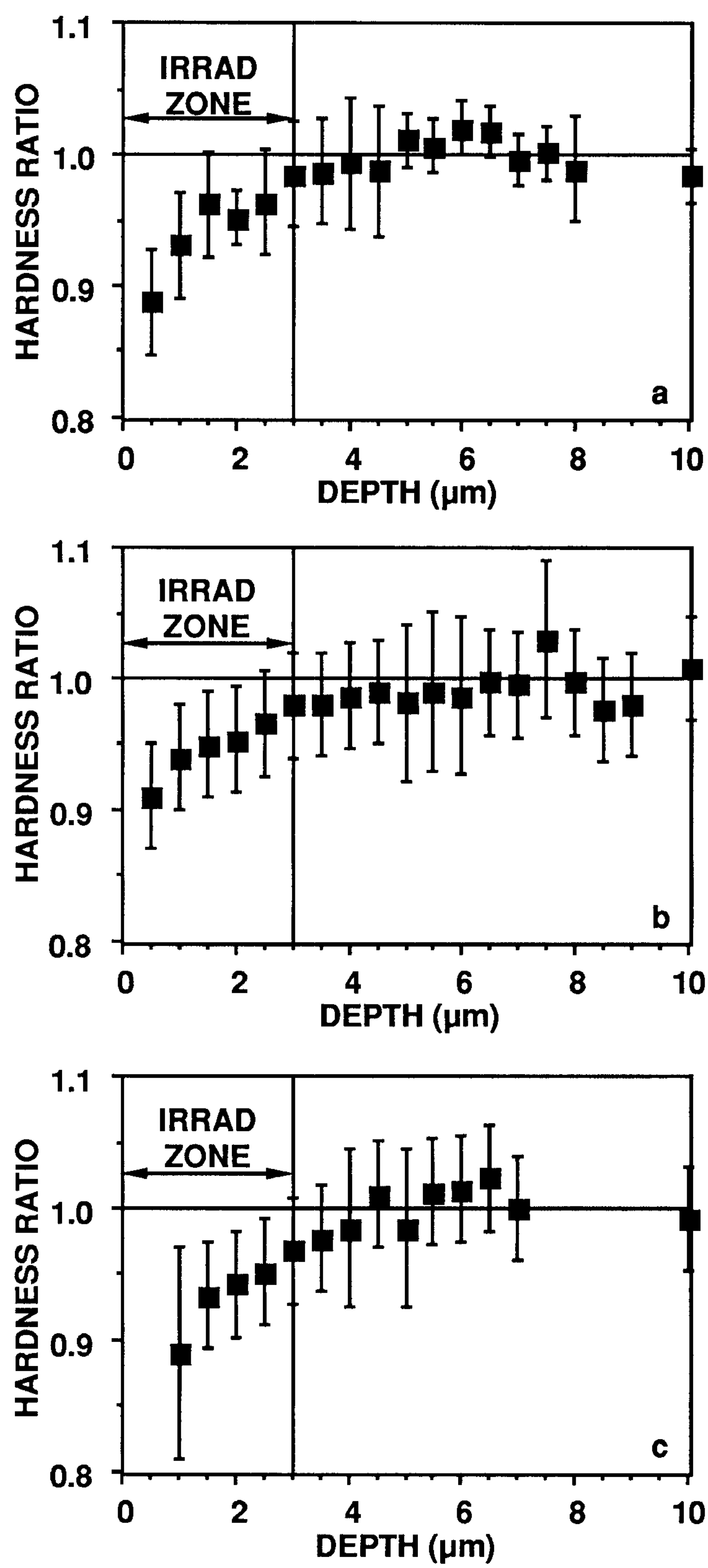

Fig. 2—Ratio of hardness to average unirradiated hardness versus depth from the irradiated interface for solution-annealed and aged Cu-Ni-Be irradiated at 300°C (a), 400°C (b) and 500°C (c).

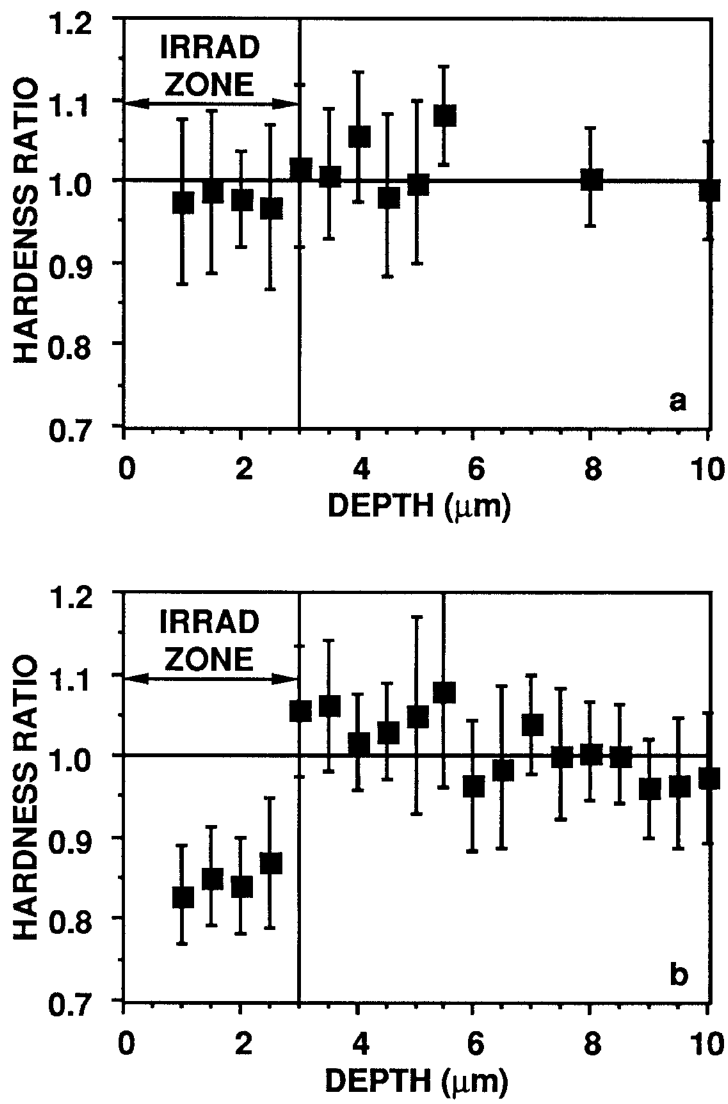

Fig. 3—Ratio of hardness to average unirradiated hardness versus depth from irradiated interface for cold-woked and aged Cu-Ni-Be irradiated at 400°C (a) and 500°C (b).

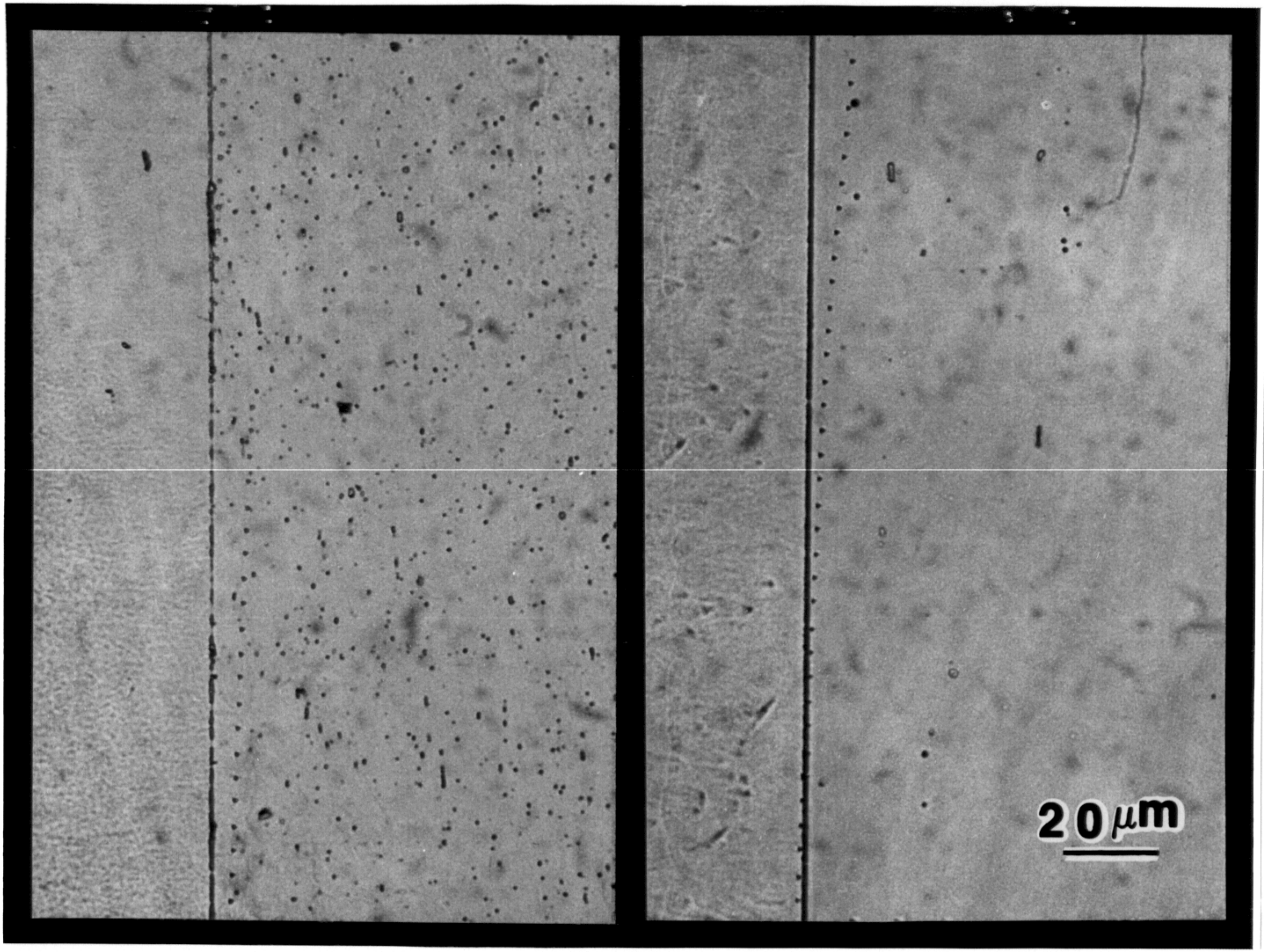

Fig. 4—Optical micrographs of indentations made in cross-sectioned samples of cold-worked and aged (left) and solution-annealed and aged (right) Cu-Ni-Be irradiated at 500°C. Copper plating is to the right and the Cu-Ni-Be to the left of the interface in each micrograph.